

WHAT IS CLAIMED IS:

- 1 1. A method for making an inorganic/organic hybrid nanolaminate barrier film,
2 comprising:
3 combining an alkoxide, an alcohol, water dilute HCl and heating the resulting
4 mixture. Introducing a coupling agent to the mixture,
5 introducing a surfactant to the mixture in a quantity sufficient that the initial
6 surfactant concentration is below the critical micelle concentration;
7 adding to the mixture one or more polymer precursors suitable for the formation of a
8 polymer selected from the group of, polyethylene naphthalate (PEN), polyether
9 etherketone (PEEK), polyether sulfone (PES), fluorinated or non-fluorinated styrene
10 polymer precursors, fluorinated or non-fluorinated methyl styrene polymer precursors,
11 fluorinated or non-fluorinated (meth)acrylate polymer precursors, and combinations
12 and/or derivatives of two or more of these precursors;
13 adding a cross-linker agent and an initiator to the mixture;
14 coating a substrate with the mixture; and
15 allowing the alcohol to evaporate so that the sol forms a film having alternating
16 organic and inorganic layers.

- 1 2. The method of claim 1 further comprising incorporating one or more hydrophobic
2 groups into the polymer precursors or eliminating one or more hydrophobic groups
3 from the polymer precursors to increase and/or decrease the hydrophobicity of the
4 organic layers.

- 1 3. The method of claim 2 wherein the one or more hydrophobic groups are selected from
2 the group of non-polar hydrophobic groups, methyl groups, benzyl (aromatic) groups,
3 PO_4^{3-} , SO_4^{2-} , CH_3COO^- , Cl^- , Br^- , NO^- , ClO_4^- , I^- , SC_n^- anions, NH_4^+ , Rb^+ , K^+ , Na^+ , Cs^+ ,
4 Li^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} cations, tryptophan, isoleucine, phenylalanine, tyrosine, leucine,
5 valine, methionine, alanine

- 1 4. The method of claim 3 wherein the surfactant includes one or more Gemini
2 surfactants.

- 1 5. The method of claim 1 wherein the alkoxide includes tetraethylorthosilicate
2 (Si(OCH₂CH₃)₄) and the alcohol is ethanol..
- 1 6. The method of claim 5 wherein in molar ratios of the tetraethylorthosilicate, ethanol,
2 water, and HCl are present in the mixture in molar ratios of 1:3.8:1:5X10⁻⁵
3 respectively.
- 1 7. The method of claim 6, wherein the coupling agent is 7-octenyltrimethoxysilane, or
2 methacryloxypropyl trimethoxysilane.
- 1 8. The method of claim 7 wherein the surfactant is cetyltrimethylammonium bromide.
- 1 9. The method of claim 1 wherein the one or more polymer precursors include 2,6-
2 Dimethylnaphthalene, or a set of monomers such as bisphenol A and di-*para*-
3 fluorophenylsulfone.
- 1 10. The method of claim 1, further comprising annealing the film at a temperature of
2 about 125° to about 150°C or greater and/or below the lowest decomposition
3 temperature of any of the organic materials in the film.
- 1 11. The method of claim 1 wherein coating a substrate with the mixture includes
2 depositing the mixture on the substrate by dip coating, spin coating, spray coating,
3 web coating, or microgravure web coating.
- 1 12. An inorganic/organic hybrid nanolaminate barrier film, comprising:
2 a plurality of layers of an inorganic material; and
3 a plurality of layers of an organic material chosen from the group of polyethylene
4 naphthalate, polyether etherketone, polyether sulfone, polymers formed from
5 fluorinated or non-fluorinated styrene polymer precursors, fluorinated or non-
6 fluorinated methyl styrene polymer precursors, fluorinated or non-fluorinated
7 (meth)acrylate polymer precursors, and combinations and/or derivatives of two or
8 more of these precursors;
9 wherein the layers of organic material alternate with the layers of inorganic material.

- 1 13. The barrier film of claim 12 wherein the total number of organic and inorganic layers
2 in the film is between about 100 and about 1000 layers, or between about 1000 and
3 about 10,000 layers, or between about 10,000 layers and about 100,000 layers.
- 1 14. The barrier film of claim 12 wherein each of the layers of inorganic material has a
2 thickness of about 0.1 nm to about 1 nm; about 1 to about 10 nm; or about 1 nm to
3 about 100 nm.
- 1 15. The barrier film of claim 14 wherein the barrier film is substantially transparent.
- 1 16. The barrier film of claim 12 wherein the barrier film has a permeability to oxygen less
2 than about 1 cc/m²/day, 0.1 cc/m²/day, 0.01 cc/m²/day, 10⁻³ cc/m²/day, 10⁻⁴ cc/m²/day,
3 10⁻⁵ cc/m²/day, or 10⁻⁶ cc/m²/day.
- 1 17. The barrier film of claim 16 wherein the barrier film has a permeability to water vapor
2 less than about 1 g/m²/day, 0.1 g/m²/day, 0.01 g/m²/day, 10⁻³ g/m²/day, 10⁻⁴ g/m²/day,
3 10⁻⁵ g/m²/day, or 10⁻⁶ g/m²/day.
- 1 18. The barrier film of claim 12 wherein one or more of the organic layers is a
2 superhydrophobic layer.
- 1 19. The barrier film of claim 18 wherein the superhydrophobic layer includes
2 fluororalkylsilane.
- 1 20. The barrier film of claim 12 wherein the organic layers are made from polymer
2 precursors to which one or more one or more hydrophobic groups have been added.
- 1 21. The barrier film of claim 20 wherein the one or more hydrophobic groups are selected
2 from the group of non-polar hydrophobic groups, methyl groups, benzyl (aromatic)
3 groups, PO₄³⁻, SO₄²⁻, CH₃COO⁻, Cl⁻, Br⁻, NO⁻, ClO₄⁻, I⁻, SC_n⁻ anions, NH₄⁺, Rb⁺, K⁺,
4 Na⁺, Cs⁺, Li⁺, Mg²⁺, Ca²⁺, Ba²⁺ cations, tryptophan, isoleucine, phenylalanine,
5 tyrosine, leucine, valine, methionine, and alanine.
- 1 22. The barrier film of claim 12 wherein the barrier film is made from a sol including one
2 or more Gemini surfactants.

1 23. An article of manufacture, comprising:
2 an object having a surface; and
3 an inorganic/organic hybrid nanolaminate barrier film of the type set forth in claim 12
4 disposed on the surface.

1 24. The article of manufacture of claim 23 wherein the object is selected from the group
2 of optoelectronic devices, LEDs, solar cells, FETs, lasers, pharmaceutical products,
3 tablets in packages, medical devices, food products, packaged foods, beverages,
4 candies, display screens, touch panel displays, flat panel displays, electroluminescent
5 windows, windows, transparent films and coatings, electronic components, and
6 chassis for appliances used in rugged environments.

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